

Optical rotation in RbTiOAsO₄ (point group *mm*2)

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Abstract. Measurement of optical rotation in RbTiOAsO₄ (RTA) with the tilter method resulted in an optical rotation of $\varrho_{12} = +17(3)^\circ/\text{mm}$ at a wavelength of 670 nm, when a (100) sample was tilted about [001]. A tilt about [010] showed no rotation, as expected from the directional dependence of optical rotation calculated from the tensor in point group *mm*2. The absolute Miller-indices of the samples were found using X-ray anomalous scattering. The calculations with a dipole-dipole model show that the As⁵⁺-ions in RTA correlate with the main structural contribution of the optical rotation. However, there seems to be an even larger intrinsic contribution due to the Ti⁴⁺ – ions as a result of the distorted octahedral co-ordination with oxygen.

1. Introduction

The ‘non-chiral’ non-linear optical features of KTiOPO₄ – (KTP) – type crystals have been associated with the distortion of the octahedral oxygen co-ordination sphere of the Ti⁴⁺-ions. The distortion introduces a large anharmonic component to the motion of optically excited electrons of both the Ti-ion and the oxygen atoms. As a result, KTP and its derivatives possess high non-linear second harmonic efficiencies (Wang et al. 2000), i.e. the percentage of frequency-doubled light intensity in relation to that of the incident beam (see for example Haussühl 1983).

The ‘chiral’ non-linear optical features include both the Faraday effect and optical rotation. Ti⁴⁺ is the only diamagnetic ion known to produce a negative ionic Faraday rotation which is also quite large and is already an exceptional feature of Ti⁴⁺ – bearing substances (Haussühl, Effgen, 1988). The optical rotation of KTP, for example, was found to be rather large as well, although calculations on the basis of the structure and the polarizability of the

atoms (Devarajan, Glazer, 1986) failed to reach these exceptionally large values (Thomas, Tebutt, Glazer, 1991).

The measurements used to derive optical rotation involved directions where the effect was expected to be a maximum according to the symmetry of the optical rotation-tensor in the point symmetry *mm*2 of KTP. The samples are strongly birefringent in these directions, and the already difficult measurements could have been affected by surface related effects which could obscure the result.

Recently, a new technique has been developed, which allows one to measure the optical rotation by tilting a sample with respect to the wave vector (Kaminsky, Haussühl, 1990; Kaminsky, Glazer, 1996). As a result, the symmetry of such tilt scans contains information on the origin of the observed optical rotation. When a sample of point group *mm*2 is cut on (100), the sign of the optical rotation changes if the wave vector passes through [100] (see below), whereas surface-related contributions are expected not to change sign.

The tilter-method is very reliable in determining the sign of optical rotation, which needs to be known in order to compare the experimental results with computer-simulations. From this, it is hoped to understand the mechanism behind the optical rotation in KTP and its derivatives such as RTA, of which the optical rotation and the ‘absolute optical configuration’ has not been determined so far.

The aim of the present report is to measure and understand the sign and magnitude of optical rotation in RTA, which involves optical measurements in combination with X-ray investigations. The specific questions are:

- In which direction is a positive optical rotation observed, given a reference crystal structure?
- Are specific structural details of RTA explaining the sign of the optical rotation?
- Does the optical rotation of RTA compare with that of other members of the KTP family?

2. Theoretical

2.1 Absolute structure assignment

We shall use the term ‘absolute optical chirality’ (Glazer, Stadnicka, 1989), when the sign of optical rotation has been assigned to the absolute structure of a crystal. When

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¹ In recent years, so-called ‘optically active’ materials and their non-linear optical features have been described in numerous reports. The term ‘optically active’ became more and more a synonym for materials which could be used for frequency doubling of light. However, historically, this term was used to describe the rotation of polarized light (optical rotation).

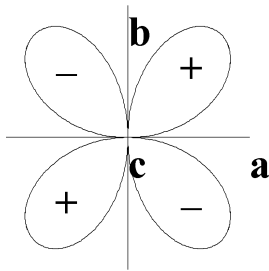


Fig. 1. Cross-section through the representation surface of optical rotation in symmetry $mm2$ where the twofold axis is along \mathbf{c} . (+) and (–) indicate the sign of optical rotation observed along the direction of the wave vector. The orientation of the physical reference system ($\mathbf{e}_1//\mathbf{a}$, $\mathbf{e}_2//\mathbf{b}$, $\mathbf{e}_3//\mathbf{c}$) depends on the Miller indices attached to the X-ray reflections of the sample (see text).

anomalous scattering of X-rays is taken into account, it is possible to distinguish between enantiomorphs of a crystal which are related by inversion symmetry and which affect the sign of chiral properties as well. The opposite enantiomorph of a quartz crystal of space group symmetry $P3_12$, for example, has the symmetry $P3_22$. In both species, the orientations of the crystallographic axes are identical, but the rotational sense of the 3-fold screw is different.

In RTA-crystals with the non-enantiomorphous point symmetry $mm2$ three operations transform between inversion-related species: a twofold-rotation about the crystallographic axis \mathbf{a} , a twofold rotation about \mathbf{b} and a mirror perpendicular to \mathbf{c} (Bierlein, Ahmed, 1987; Loiacono, Stolzenberger, 1988). The sign of optical rotation changes in all cases (see below and Fig. 1), i.e., if we look, say, along $[110]$ a simple rotation of the whole structure by 180° around \mathbf{a} , which does not invert space like a mirror operation, would apparently change the sign of the optical rotation along this direction in $mm2$, whereas in the quartz example above ($P3_12$), a rotation around $[110]$ or any other axis perpendicular to the \mathbf{c} -axis would not affect the sign of the optical rotation.

The absolute optical configuration for a given crystal structure in this case has to specify in which *direction* any, for example, positive optical rotation has been observed. A tensorial property is given in reference to the assignment of the physical reference system \mathbf{e}_i which, by convention, is related to the crystallographic axes \mathbf{a} , \mathbf{b} and \mathbf{c} (see for example Haussühl 1983), like

$$\mathbf{e}_2 // \mathbf{b}^*, \quad \mathbf{e}_3 // \mathbf{c}, \quad \mathbf{e}_1 // \mathbf{e}_2 \times \mathbf{e}_3. \quad (1)$$

The conversion of the directions of \mathbf{b} and \mathbf{c} and, thus, of \mathbf{e}_2 and \mathbf{e}_3 as introduced by a two-fold rotation about \mathbf{a} is described by a symmetry operation u_{ij}^{2-a} . The rotation about \mathbf{b} is introduced by u_{ij}^{2-b} . The mirror perpendicular to \mathbf{c} is described by a matrix u_{ij}^m . The optical rotation in $mm2$ is described by the axial tensor Q_{ij} :

$$u_{ij}^{2-a} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} u_{ij}^{2-b} = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$$

$$u_{ij}^m = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}, \quad (2)$$

$$Q_{ij} = \begin{pmatrix} 0 & Q_{12} & 0 \\ Q_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The component Q_{12} transforms with a rotation about \mathbf{a} like

$$Q'_{12} = \det(u_{ij}^{2-a}) u_{11}^{2-a} u_{22}^{2-a} Q_{12} = 1 \cdot 1 \cdot (-1) \cdot Q_{12} = -Q_{12}. \quad (3)$$

Similar, the mirror perpendicular to \mathbf{c} gives

$$Q'_{12} = \det(u_{ij}^m) u_{11}^m u_{22}^m Q_{12} = 1 \cdot 1 \cdot (-1) \cdot Q_{12} = -Q_{12}. \quad (4)$$

As a result of any of the three twin operations, the sign of optical rotation changes and the type of twinning operation is not distinguished from optical rotation, contrary to Thomas et al. (1991).

When assigning the indices to the faces of a crystal, it is convenient to calculate first the intensity-difference of scattered X-rays between pairs (hkl) and $(\bar{h}\bar{k}\bar{l})$ from the known structural model:

$$\Delta I/I = \frac{I(hkl) - I(\bar{h}\bar{k}\bar{l})}{\frac{1}{2}(I(hkl) + I(\bar{h}\bar{k}\bar{l}))}. \quad (5)$$

This helps to find out, which of them are significant before starting to collect the X-ray intensity data. The published crystal structure (Thomas, Mayo, Watts, 1992) was taken as a reference. The calculated differences, using the program ‘Crystallographica’ (Oxford Cryosystems), are listed in Table 1. If the experiment shows the same differences, the assignment of indices in the X-ray data can be taken as absolute. If the differences consistently exhibit the opposite sign, the indices have to be inverted to match the reference structure.

Table 1. Observed and calculated Friedel differences for the RTA-sample used in the optical rotation and X-ray anomalous scattering experiment. The calculated differences are based on the structural model published in Thomas, Mayo and Watts (1992). Errors are given in parentheses.

$h k l$	$I(hkl)$	$I(\bar{h}\bar{k}\bar{l})$	$\Delta I/I^{\text{observed}} (\%)$	$\Delta I/I^{\text{calculated}} (\%)$
0 0 4	2232(13)	2474(14)	–10.3(8)	+10.8
0 0 8	688(7)	617(7)	+10.8(1.5)	–13.7
1 1 4	340(5)	435(6)	–24.5(1.8)	+18.8
0 2 4	890(8)	1129(8)	–23.7(1.1)	+26.2
2 2 7	259(5)	173(4)	+39(3)	–21.8
1 2 10	76(4)	63(4)	+19(8)	–12.8
1 2 6	62(4)	44(4)	+34(10)	–24.8
1 1 10	40(4)	32(4)	+25(15)	–21.6
1 1 6	133(4)	102(4)	+26(5)	–17.0
2 1 9	52(4)	35(4)	+38(13)	–25.0

2.2 Calculation of optical rotation

Optical properties may be calculated on the basis of atomic positions \mathbf{r}_S and individual isotropic electronic polarizabilities α_S , assigned to the atoms in a structure, labelled with index S . The theory of dipole-dipole interaction has been described elsewhere (Ewald, 1921; Born, Goepfert-Mayer, 1933; Beurskens-Kerssen, Kroon, Endemann, van Laar, Bijvoet, 1963; van Laar, Endeman, Bijvoet, 1968).

Here, we like to present the final equation (Devarajan, Glazer, 1986) from which the optical rotation $\rho(\mathbf{k})$ in direction of the wave vector \mathbf{k} and the coefficients of the dielectric tensor ε_{ij} at optical frequencies are calculated: $e_{rij} = \text{Levi-Civita symbol}$, $k_r = \text{components of the wave vector}$, $n = \text{average refractive index}$, $\nu = \text{volume of the unit cell}$, $\delta_{ij} = \text{Kronecker symbol}$):

$$\rho(\mathbf{k}) = \frac{-e_{rij}k_r}{2n\nu} \text{Im} \sum_{SS'} (C_{SS'})_{ij},$$

$$\varepsilon_{ij} = \delta_{ij} + \frac{1}{\nu} \sum_{SS'} (C_{SS'})_{ij}. \quad (6)$$

$$C_{SS'} = (\alpha_S^{-1} \delta_{SS'} - Q_{SS'})$$

with

$$Q_{SS'} = Q_{SS'}^0 + i \sum_{\gamma} Q_{SS'}^1 k_{\gamma}$$

$$Q_{SS'}^0 = -\frac{1}{\varepsilon_0 \nu R^2} \sum_{\mathbf{h}} h_{\alpha} h_{\beta} G e^{i\mathbf{h}(\mathbf{r}_S - \mathbf{r}_{S'})}$$

$$+ \frac{R^3}{4\pi\varepsilon_0} \sum_{\mathbf{h}} H_{\alpha\beta}(\mathbf{R}\mathbf{r}_{SS'}^{\prime\prime}) + \delta_{\alpha\beta} \delta_{SS'} \frac{R^3}{3\varepsilon_0 \pi \sqrt{\pi}}$$

$$Q_{SS'}^1 = -\frac{1}{\varepsilon_0 \nu R^2} \sum_{\mathbf{h}} \left[(h_{\alpha} \delta_{\beta\gamma} + h_{\beta} \delta_{\alpha\gamma}) \right.$$

$$\left. + \frac{2}{R^2} h_{\alpha} h_{\beta} h_{\gamma} G' e^{i\mathbf{h}(\mathbf{r}_S - \mathbf{r}_{S'})} \right] - \frac{R^3}{2\pi\varepsilon_0} \sum_{\mathbf{h}} H_{\alpha\beta}(\mathbf{R}\mathbf{r}_{SS'}^{\prime\prime}) \mathbf{r}_{SS'}^{\prime\prime}$$

$$G = \frac{\exp(-h^2/R^2)}{h^2/R^2}, \quad G' = \partial G / \partial k_{\gamma},$$

$$H_{\alpha\beta}(\mathbf{x}) = \frac{x_{\alpha} x_{\beta}}{x^2} \psi(|\mathbf{x}|) - \delta_{\alpha\beta} \Phi(|\mathbf{x}|),$$

$$\psi(|\mathbf{x}|) = 3\Phi(|\mathbf{x}|) + \frac{4e^{-|\mathbf{x}|^2}}{\sqrt{\pi}},$$

$$\Phi(|\mathbf{x}|) = \frac{1}{|\mathbf{x}|^3} \text{erfc}(|\mathbf{x}|) + \frac{2e^{-|\mathbf{x}|^2}}{\sqrt{\pi}},$$

$$\mathbf{r}_{SS'}^{\prime\prime} = \mathbf{r}^{\prime\prime} + \mathbf{r}_{S'} - \mathbf{r}_S. \quad (7)$$

Indices α , β and γ refer to a Cartesian reference system and R is a parameter chosen so as to ensure convergence. The term corresponding to unit cell index $l' = 0$ with $S = S'$ is ignored in the summation over l' and in the summation over face-normal vector \mathbf{h} , the term $\mathbf{h} = (000)$ should be omitted.

The dipole-dipole interaction effectively causes the polarizabilities of the atoms to become anisotropic according to the effective polarizability $\alpha_{S,ij}$ of atom s , calculated from $(C_{SS'})_{ij}$:

$$\alpha_{S,ij} = \text{Re} \sum_{S'} (C_{SS'})_{ij}. \quad (8)$$

This theoretical model calculates optical rotation on the basis of the interacting forces reliably in an inorganic structure. It was applied successfully to molecular crystals as well, where the optical rotation results from the interacting fields within a molecule and where those between the molecules are less significant (Kaminsky, Glazer, 1997). However, the theory was designed, using point dipoles to represent the relevant feature of the atoms with

respect to optical phenomena. Thus, if there are specific chiral contributions of the atoms themselves to optical rotation, we may need to add these in the form of empirical numbers to the value of optical rotation which is calculated with the dipole-dipole model.

3. Experimental

3.1 X-ray studies and sample orientation

The crystalline RTA-material was flux-grown by the method of Jacco, Loicano, Jaso, Mizell and Greenberg (1984). A (100) section was cut from a single crystal using a diamond-coated saw and ground into a thin plate of 0.17 mm thickness, using emerald paper. The faces of the plates where then polished down to optical quality.

To derive the absolute Miller-indices, a sample was marked as shown in Fig. 2a and centred on a Stoe Stadi-4 four-circle diffractometer. Reflections were investigated where face normals of the reflecting planes were close to the plane of the sample, i.e. low index h and high index k or l . Thus, all the X-rays passed through the sample plate at a small angle towards the plate normal and experienced a similar absorption (Fig. 2b).

On the basis of the orientation matrix found by centring the sample on the diffractometer, the intensity differences observed were recorded for positive and negative 2θ settings.

The measurements were repeated with indices h or k inverted to observe the effect of normal X-ray absorption. The final result is listed in Table 1. The observed intensity differences were found to be consistently opposite to the calculated values. As a result, the indices used in the X-ray measurement had to be inverted to be in accord with the crystal structure, used for the calculations. The sample was then removed from the diffractometer and inserted into the tilter-system to measure the optical rotation. The orientation of the sample was such that the wave vector \mathbf{k} was parallel to $[\bar{1}00]$. The tilt axis \mathbf{t} of the device (see below) was aligned to be parallel to $[001]$ and a rotation about that axis \mathbf{t} , when assigned to a positive tilt angle α of the sample, effectively moved the wave vector towards $\mathbf{x} // [0\bar{1}0]$ by an angle β inside the sample (see Fig. 2a).

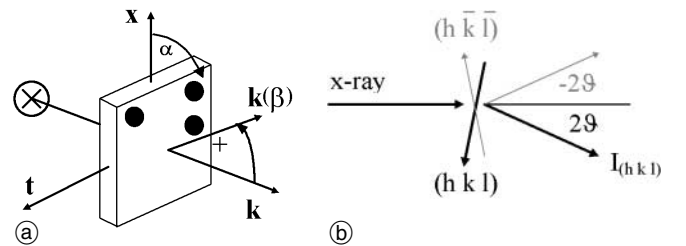


Fig. 2. (a) The orientation of a marked sample with respect to the laboratory reference system: tilt-axis \mathbf{t} , wave vector \mathbf{k} , and $\mathbf{x} = \mathbf{t} \times \mathbf{x}$. The wave vector moves along the arrow by $+\beta$ as a result of tilting the sample by a tilt angle $+\alpha \dots$ (b) The Bragg-condition is satisfied in two settings for 2θ (black and grey) which allows one to access a Friedel-pair with a similar X-ray absorption.

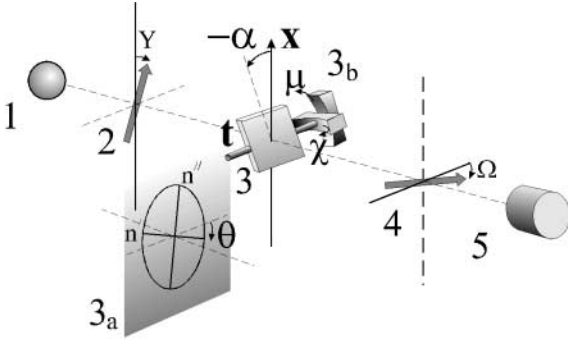


Fig. 3. Principal components of the tilter system (Kaminsky, Glazer, 1996). The set-up consists of the usual components of a polarimeter (lamp [1], polarizer [2], analyser [4], detector [5]). The polarizer can be rotated by a stepper motor through an angle Y of maximum $\pm 10^\circ$ with a resolution of $0.014(1)^\circ$. The crystal plate [3] is tilted by a stepper motor through $\pm 27.0(1)^\circ$. It is also mounted in a two-circle goniometer arrangement [3b] to enable proper orientation of the sample. The sample can be heated and shifted by a translation stage to change its position relative to the incident beam of about $50 \mu\text{m}$ diameter. The shape of the optical indicatrix section [3a], determined by the birefringence ($n'' - n'$) and orientation angle θ , depends on the tilt angle. The analyser system consists of a removable quarter-wave compensator and a Pockels-ADP ($\text{NH}_4\text{H}_2\text{PO}_4$)-modulator, capable of computer-controlled rotation Ω of $\pm 0.8^\circ$ with a resolution of $0.0004(1)^\circ$.

3.2 Measurement of optical rotation

The tilter is an optical device, where all parameters describing the optical indicatrix in a crystal and its optical rotation are simultaneously measured by tilting the sample and detecting the intensity of incident linearly polarized light as a function of the analyser angle (Kaminsky, Haussühl, 1990) or analyser and polarizer angles (Fig. 3, Kaminsky, Glazer, 1996).

The observed rotation of polarized light $\varphi(\alpha)$ of a (100)-cut sample plate in symmetry $mm2$, when tilted by α , varies with angle β of the wave vector towards the plate normal inside the sample, $\Delta n(\beta)$ birefringence normal to the wave vector, like (see for example: Kaminsky and Haussühl, 1993)

$$\varphi(\alpha) = \varphi_0(\beta) \frac{\sin \delta}{\delta}; \quad \varphi_0 = L(\beta) \varrho_{12} \sin \beta \cos \beta;$$

$$\delta(\alpha) = \frac{2\pi}{\lambda} L(\beta) \Delta n(\beta) = \text{retardation}. \quad (9)$$

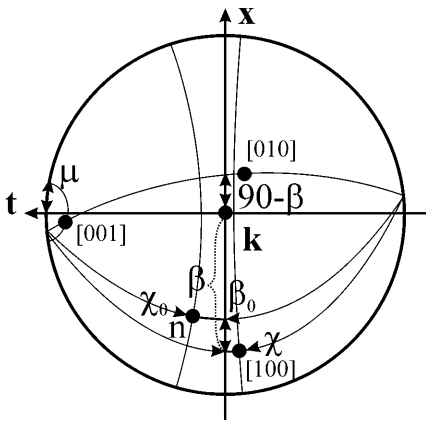


Fig. 4. Stereographic projection showing the adjustment of a marked crystal in the tilter set-up. \mathbf{n} is the sample's plate normal, \mathbf{t} is the tilt axis, \mathbf{k} is the wave vector, $\mathbf{x} = \mathbf{t} \times \mathbf{k}$. The X-ray experiment revealed that \mathbf{k} is $\parallel [100]$, $\mathbf{t} \parallel [001]$ and $\mathbf{x} \parallel [010]$.

We have the interesting case that the rotation changes sign when passing through the $[100]$, $[\bar{1}00]$, $[010]$ or $[0\bar{1}0]$ directions within the (001) – plane (Fig. 1). Rotating the sample about one of these directions changes sign of the slope as well. This enables one to use the tilter to get the optical rotation from the difference of two measurements on a single (100) – cut sample plate. However, it is very important to make sure that the crystal is adjusted as well as possible with respect to the following small deviations from a perfect adjustment for the case described above (Fig. 4):

- the angle χ between the wave vector \mathbf{k} and $[100]$ in RTA,
- the angle χ_0 between plate-normal \mathbf{n} and the wave vector \mathbf{k} in the $\mathbf{t} - \mathbf{k}$ plane,
- the angle β_0 between the plate-normal \mathbf{n} and the wave vector \mathbf{k} within the tilt-plane $\mathbf{t} - \mathbf{x}$ inside the sample, when the sample is tilted so that β is $= 0$,
- the angle μ between $[001]$ of RTA and tilt axis \mathbf{t} .
- the offset o between the centre of the tilt axis and the middle between the surfaces of the crystal, i.e. the error introduced when the tilt axis does not go through the crystal.

Furthermore, to avoid a too large beam walk-off effect, the entrance diaphragm in front of the photodetector needs to be small, cutting out about half of the intensity. All the angles mentioned had at least to be smaller than 0.3° to avoid problems. Here, it was helpful that the tilter method allows one to derive most of the adjustment parameters from the measurement itself. Artefact effects of about 10° in the optical rotation were observed, when χ is about 0.8° and up to 30° for $\chi = 1.3^\circ$. For $\chi < 0.3^\circ$ the parasitic effect is estimated to be smaller than 1° . Similar, but less large, effects are related to errors in β_0 , μ , χ_0 , and o .

The (100)-cut provided was prepared and oriented well enough to satisfy the conditions outlined above. Fig. 5 shows a scan of the so-called ‘ellipticity’ $\varphi(\alpha) \delta^{-1} \sin \delta$ through $[\bar{1}00]$ with the tilt axis \mathbf{t} along $[001]$ as results

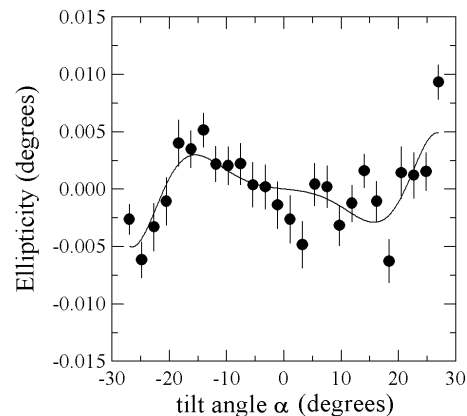


Fig. 5. A typical plot of the so-called ‘ellipticity’ $\varphi(\alpha) \sin \delta(\alpha) / \delta(\alpha)$ of a (100)-cut RTA sample with tilt axis along $[001]$ plotted against the tilt angle α . The optical rotation is $\varphi(\alpha) = \varrho_{12} L' \sin \beta \cos \beta$, ϱ_{12} is the optical rotation. L' is the thickness of the sample as it varies with the tilting and β is the angle between the wave vector and the plate normal vector inside the crystal. $\varrho_{12} = 17(3)^\circ \text{mm}^{-1}$. The value of $\sin \delta / \delta$ was negative for tilt angles between $+20^\circ$ and -20° in this example.

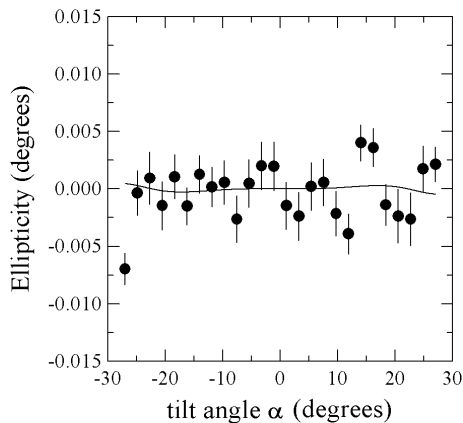


Fig. 6. A typical plot of the ‘ellipticity’ of a (100)-cut RTA with tilt axis along [010] (tilt **b**, Fig. 4), plotted against the tilt angle α . $\varphi(\alpha)$, see above. $\varrho_{13} = (4)^\circ \text{ mm}^{-1}$, confirming its absence in the optical rotation tensor.

from a final refinement of the measurement (see Kaminsky, 1997). Fig. 6 shows an equivalent scan with the tilt axis along [010]. This scan avoids optically rotatory directions and serves as a test of the procedure.

The statistical error (20%) is about the same as the systematic error in the measurements of Fig. 5 and Fig. 6. The final result is $\varrho_{12} = 17(3)^\circ/\text{mm}$, where two measurements related by a rotation about [100] by 180° have been used to eliminate any problems as much as possible. The error of 3° is estimated to be the total error. Twinning was not observed in this sample. The rotation was found to be positive in the $-\mathbf{a}/-\mathbf{b}$ section, and thus also in the section \mathbf{a}/\mathbf{b} .

Because the function with which the optical rotation varies in a (100)-cut sample is of odd order in α , the even-shaped parasitic contributions with respect to the tilt angle α are separated out very effectively.

A negative rotation was found along $[\bar{1}20]$ in a different sample, which confirms the result obtained above. The measurement of the magnitude of the rotation, however, was less accurate.

4. Discussion

4.1 Experimental results

In general, experiments on optical rotation, like those described here, are reliable to within an optical rotation of $50^\circ/\text{mm} \times \Delta n$. Along [100] the birefringence Δn for a wavelength of 670 nm is 0.0812, and along [120] $\Delta n = 0.0842$ (Fenimore, Schepler, Zelmon, Kück, Ramabadran, von Richter, Small, 1996). The reliability of a single optical rotation measurement thus is about $4^\circ/\text{mm}$. This compares well with the error derived experimentally, which is a little smaller since the result could be refined from the difference of two tilt scans. The sign of the optical rotation has non-ambiguously been derived and assigned to the absolute structure of RTA.

In using the tilter method, we were able to see the sign-change of optical rotation in point group *mm*2 when the wave vector passes through the crystallographic **a** or **b** axes. Very few similar experiments have been carried out so far (in crystals which are optically isotropic at selected

Table 2. Optical rotation of KTP-type crystals for 670 nm.

Substance	Optical rotation ϱ_{12} ($^\circ/\text{mm}$)	Reference	Experimental method
RbTiOAsO ₄	17(3)	this paper	tilter method
KTiOPO ₄	20(3)	Thomas et al. 1991 (see text)	Wavelength-scanning HAUP
RbTiOPO ₄	18(4)	Tebutt (1991)	Wavelength-scanning HAUP
KTiOAsO ₄	Positive sign	Lingard et al.	Wavelength-scanning HAUP

wavelengths: Hobden, M.V. 1968, 1969; Kim, Griewatsch and Küppers 1993; in crystals which have no optical isotropic wavelength in the visible light spectrum and no optic axes related by mirror-symmetry: Kaminsky, 1997; Mucha, Stadnicka, Kaminsky, Glazer, 1997).

A problem arises when comparing the sign of optical rotation of RTA with that of other members of the KTP family, i.e. KTP itself, as published (Thomas et al., 1991). The results seem to carry different signs which was unexpected (see calculations below). The X-ray experiments described here and of the cited paper were similar so that we can expect that the Miller-indices of the samples were correctly assigned. Recently it was shown how to unambiguously derive the sign of optical rotation from scans with respect to wavelength (for details, see Lingard and Renshaw, 1994). In revising the original wavelength scans of the so-called ‘ellipticity’ in KTP, we found a positive optical rotation along $[xy0]$, with x and y having the same sign, which equals the optical rotation in RTA (Table 2).

It was not possible to identify any chiral axis in RTA to which optical rotation could be related and interpreted the way it was demonstrated earlier (Glazer, Stadnicka, 1986). If optical rotation is correlated with single structural units like those of the AsO₄-tetrahedra, they have to be arranged in a special way. There is for example no chirality of a regular AsO₄-unit for a wave vector being directed along one of the As–O bonds. As another example for the effect of tetrahedral orientation on optical rotation, we can take the Cd-langbeinite where we found a strong increase in optical rotation along several directions in K₂Cd₂(SO₄)₃ when the SO₄-tetrahedra became slightly tilted as a result of the cubic/orthorhombic phase transition at 432 K (Kaminsky, 1996).

The AsO₄-tetrahedra in the RTA-structure in a projection along [120] revealed no preferred rotational sense since left and right handed tetrahedron come in quasi mirror-symmetric pairs. Thus, we have to assume that very small differences in orientation of each tetrahedron within a pair are responsible for the As⁵⁺-related optical rotation because of which their contribution to optical rotation is not completely balanced.

4.2 Model calculations

The semi-empirical model calculations take the experimental refractive indices as a reference. The electronic polariz-

Table 3. Polarizability volumes α_S (\AA^3), calculated refractive indices n_a , n_b , n_c along the crystallographic axes and calculated optical rotation ρ_{12} ($^\circ/\text{mm}$). The experimental refractive indices for a wavelength of 670 nm are $n_a = 1.8255$, $n_b = 1.8336$, $n_c = 1.9118$ with variance on the last given digit (Fenimore et al., 1996). The first line shows refractive indices calculated with polarizability volumes from Tessman, Kahn and Shockley (1953), see text for the choice of the value for As^{5+} , which is not part of that publication. The Rb-polarizability does affect optical rotation only a little.

α_{As}	α_{Ti}	α_{Rb}	α_{O}	n_a	n_b	n_c	ρ_{12}
0.3	0.2	1.8	2	1.898	1.912	1.909	4.34
0.1	0.6440	1.0237	1.8921	1.837	1.823	1.911	0.34
0.3	0.6557	1.0823	1.8080	1.837	1.829	1.905	1.18
0.5	0.8035	1.0014	1.6505	1.831	1.825	1.915	2.71
0.7	0.8412	1.0039	1.5346	1.829	1.832	1.911	4.37
0.9	0.9235	0.9298	1.3972	1.825	1.834	1.912	6.19

ability volumes of the atoms in the structure are modelled until the refractive indices of the calculation are close to the measured values. With at least four different types of atoms in RTA and only three refractive indices with fixed polarizations, we need to set one, namely α_{As} , and fit the other three to the refractive indices. Thus, we find several different sets of polarizabilities with which the refractive indices are calculated. The parameters and outcome of the calculations are shown in Table 3.

Before modelling the polarizabilities, we first tried out the set of parameters taken from Tessman, Kahn and Shockley (1953). The value for As^{5+} , which is not part of that publication, was found to fit the optical rotation in $(\text{NH}_4)_2\text{H}_2\text{AsO}_4$ (for a compilation of optical rotation measurements and other aspects on circular birefringence see: Kaminsky, 2000). Obviously the optical rotation is calculated to be much smaller than the experimental value and the calculated birefringence is wrong, although the average refractive index compares well with the experimental result.

The polarizability of Ti^{4+} increased significantly when fitting the experimental refractive indices, but then the calculated optical rotation decreased notably. In varying the polarizability of the As^{5+} -ion we see a strong correlation with optical rotation. In addition it was not possible to calculate n_a to be smaller than n_b when the polarizability of the As^{5+} -ions was kept small. This could be explained by the model calculations being entirely classical in nature. The selection rules, which govern the shape of absorption spectra, are not included and thus, the calculated birefringence could deviate from the experimental values significantly although the polarizabilities may be well selected.

The best fit to the experimental refractive indices was obtained for a polarizability of the As^{5+} larger than 0.7\AA^3 . Such a high polarizability seems to be physically meaningless, although large cationic polarizabilities have been used before to calculate optical properties, i. e. Si^{4+} in low-quartz.

As there is no physically acceptable set of parameters which is consistent with the refractive indices and the experimental optical rotation at the same time, which we take as reliably determined, we need to consider other sources of optical rotation. One possibility is that the oxy-

gens of the tetragonal co-ordination of the As^{5+} -ion are more strongly polarized than those which connect the Ti-octahedra, in which case a larger optical rotation may be possible. In such a calculation we would have to introduce an additional unknown variable to the already large set of parameters, and that was considered to be unjustifiable. Another source of optical rotation is any contribution by a non-centrosymmetric electron density surrounding a single atom. The absence of a symmetry-centre of such arrangements is sufficient for molecular optical rotation if not counterbalanced by symmetry-equivalent pairs of them in the structure. The most likely candidate for such a contribution is the Ti^{4+} -ion because the symmetry of the octahedral co-ordination sphere is slightly broken which expresses itself in a significant anisotropic polarizability. This 'intrinsic' optical rotation of the Ti^{4+} -ion as a result of the symmetry of its co-ordination shell would have to carry a much higher optical rotation than the structural contribution.

Finally, if we assume that the polarizability of P^{5+} is smaller than that of As^{5+} , we would expect a difference to optical rotation within the contribution range of the tetrahedra in RbTiOPO_4 of a few degrees per millimetre. The variation of the experimental results is very small indeed (Table 2) which supports the idea of an intrinsic optical rotation of the Ti^{4+} -ion of about $15^\circ/\text{mm}$ for the KTP – type crystals.

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